



Synthesis and characterization of a composite of polyaniline and carbon black

R. Del RÍO¹, J.H. ZAGAL^{1*}, G.de T. ANDRADE² and S.R. BIAGGIO²

¹Universidad de Santiago de Chile, Departamento de Química Aplicada, Casilla 40 – Correo 33, Santiago, Chile;

²Universidade Federal de São Carlos, Departamento de Química, São Carlos-SP, Brasil

(*author for correspondence, e-mail: jzagal@lauca.usach.cl)

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Abstract

A method is described for obtaining a composite of polyaniline and carbon black by cycling the potential of a Pt electrode in a solution containing aniline and carbon black suspension. The solution may also contain sodium dodecyl sulphate (SDS) as additive. It is shown that the rate of polymerization is enhanced by the presence of both carbon black and SDS by a factor of 5. The composite was characterized by cyclic voltammetry, scanning electron microscopy and capacity measurements.

1. Introduction

Polyaniline has received a great deal of attention in the last two decades as it was the first conducting polymer whose electronic properties could be reversibly controlled by both charge transfer doping and protonation [1–3]. These properties make polyaniline a versatile material with applications as varied as active electrodes in batteries [4], in microelectronics [5, 6], as electrochromic material for displays [7, 8], sensors [9] and in electrocatalysis [10, 11]. The low weight of polyaniline and other conductive polymers compared to that for metals is one of the advantages of these materials for applications in energy conversion devices. Polyaniline has been studied as electrode material for lithium batteries [12], but only few reports show high charge–discharge capacities. Composites of conductive polymers are attractive because they can combine the properties of the conducting polymer with the properties of other compounds. Inclusion of platinum particles is an example of a composite, in which particles of the metal, together with other compounds are included in the polymer matrix [13]. Composites of polyaniline and Pt have shown high catalytic activity for the oxidation of methanol and other reactions and are more resistant to contamination with by-products compared to the pure metal [10].

The synthesis of composites of polypyrrole and carbon black has also been reported [14]. These composites have been electrosynthesized from aqueous media containing the monomer and a dispersion of carbon black. Polymerization of pyrrole has been induced by applying a constant current, a constant potential, or cycling the potential during the synthesis [15]. Whatever electrochemical method is used, the negatively charged carbon black particles migrate towards the positively charged anode, and become embedded in the growing polymer matrix. The resulting composite is a three-dimensional assembly of dispersed carbon inside the conductive polymer medium [15]. The electrochemical methods offer an advantage over the methods involving the chemical oxidation of the monomer in the sense that the composite is obtained as a coating on a conductive electrode support. This is specially important in applications such as batteries, electrocatalysts and sensors.

To the best of our knowledge there are no reports in the literature on carbon composites using polyaniline as a conductive polymer. In this paper we report the synthesis of a composite of carbon black and polyaniline on Pt electrode, obtained potentiodynamically in acid electrolyte containing aniline and a suspension of carbon black. We show that these composites can be conveniently synthesized from acid media in the presence of additives and that the resulting materials have enhanced charge storage characteristics.

2. Experimental details

Aniline was used as aniline hydrochloride (analytical grade from Aldrich). H_2SO_4 , HCl and sodium dodecyl sulphate (SDS) additive were analytical grade from Merck and used without further purification. Carbon black was Vulcan XC-72 from Cabot. Doubly-distilled deionized water was employed for preparing all solutions. Polyaniline-carbon black (Pani-CB) composites were electrosynthesized on a platinum foil (99.99% from Aldrich) exposing 2 cm^2 of geometrical area. The counter electrode, a 99.99% platinum coil, was separated from the main compartment by fritted glass. A saturated calomel electrode (SCE), separated from the working electrode compartment by a Luggin probe, was used as reference. Both synthesis and impedance measurements were performed under nitrogen at 20°C . A single compartment glass cell was used for the impedance measurements. In this case, the counter electrode was a cylinder of Pt grid surrounding the working and reference electrodes.

Pani-CB composites were synthesized in deaerated 1 M HCl containing varying amounts of carbon black in suspension. SDS was used as additive in order to improve the stability and electroactivity of the films [16]. The potential of the Pt working electrode was cycled between -0.2 and 0.8 V for 100 cycles at 0.1 V s^{-1} , while stirring the electrolyte. Composites synthesized with SDS in the electrolyte were analysed by electrochemical impedance spectroscopy (EIS) measurements in fresh $0.5\text{ M H}_2\text{SO}_4$ solutions without the monomer. The choice of the measuring electrolyte was to make possible comparisons with our previous works [17, 18]. The composite electrosynthesis itself was not performed in H_2SO_4 solutions in order to avoid misinterpretations on the effect of a possible S-species incorporation (from SDS) in the film. The frequency range extended from 10 mHz to 10 kHz and an a.c. potential perturbation of 10 mV r.m.s. was used. The frequency response was measured under steady-state potentiostatic conditions at -0.2 , -0.1 , 0.0 , 0.1 , 0.2 , 0.3 and 0.4 V . The electrosynthesis was conducted using a POS73 Wenking Potentiostat and the polymer growth was monitored on a 2000 Omnigraphic Houston X-Y recorder. The frequency response analyser was an EcoChemie Autolab Pgstat20 and data acquisition was computer assisted via the Eco Chemie FRA software.

3. Results and discussion

3.1. Electrosynthesis of the polyaniline-carbon black composites

It is known that SDS increases the rate of chemical polymerization of aniline [19, 20]. The role of carbon black and SDS additive in the electrosynthesis of Pani is discussed in Figures 1–3. Figure 1 illustrates the potentiodynamic response of two Pani films prepared in the presence or absence of additives in the electrolyte. Figure 1(a) shows the response of a Pani film obtained after 100 cycles of potential at 0.1 V s^{-1} between -0.2 and 0.8 V without additives. The charge under the anodic peak is about 10 mC cm^{-2} . Figure 1(b) shows the potentiodynamic response of a composite obtained with 1 g L^{-1} carbon black and $5 \times 10^{-3}\text{ M}$ SDS, which exhibits a much larger anodic electrical charge (140 mC cm^{-2}). Moreover, the Pani-CB films show current peaks which are more rounded than in the case of Pani only, and the redox-peaks separation for Pani-CB is 0.3 V , compared to 0.15 V for Pani film. This might reflect a larger resistance of the former, possibly due to its larger thickness and different morphology.

The effect of carbon black (CB) content in the forming electrolyte on the anodic electrical charge for the film deposition was studied for several composites Pani-CB. As shown in Figure 2, the rising part of the curve is expected, since more CB particles are present in the electrolyte to enhance Pani polymerization. However, a decrease in the anodic peak current is observed for concentrations of CB in the suspension larger than about 2 g L^{-1} , due to the loss of a part of the poorly adherent film formed under those conditions. Using more than 1 g L^{-1} leads to mechanically unstable films that crack when dry. This result essentially indicates that no benefits are obtained by using larger concentrations of CB in the forming electrolyte. Consequently, for the remaining experiments, all films were prepared with 1 g L^{-1} of CB in the electrolyte. The dispersion of the data observed in the plot of Figure 2 is a result of irreproducibilities arising from the composite preparation technique, specifically the carbon black powder under mechanical stirring.

Figure 3 shows the variation of the anodic current peak with the number of cycles, which illustrates the rate of Pani growth obtained with and without additives. At the initial stage of polymerization, all Pani films grow at the same rate. After about 35 voltammetric cycles, the films with additives grow much faster. This is probably not due to a catalytic effect but rather to an area effect as a result of the presence of CB,

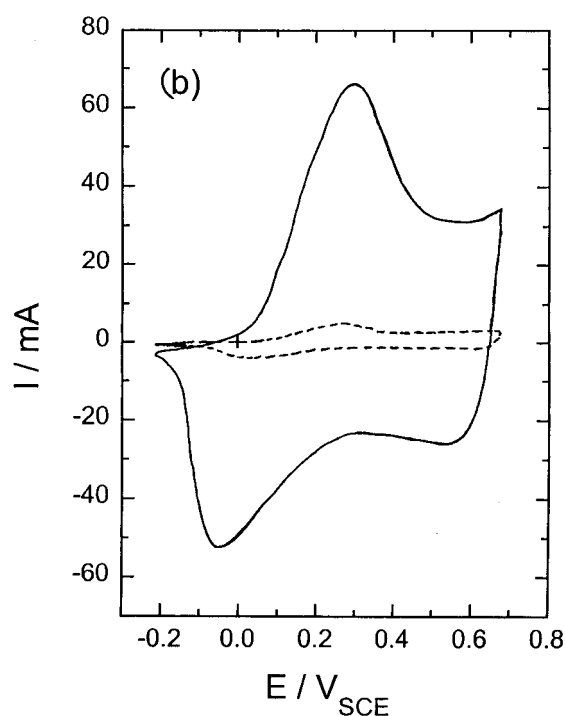
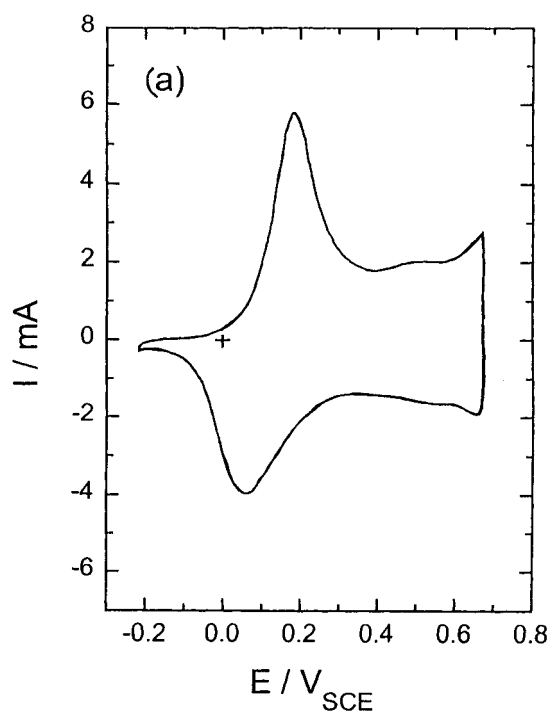


Fig. 1. Voltammetric profiles of Pani films synthesized after 100 CV cycles in: (a) 0.1 M aniline and 1.0 M HCl and (b) 0.1 M aniline, 5×10^{-3} M SDS, 1.0 M HCl and 1.0 g L^{-1} of carbon black under stirring. The CV profiles were recorded in $0.5 \text{ M H}_2\text{SO}_4$. Key (b): (---) Pani and (—) Pani CB.

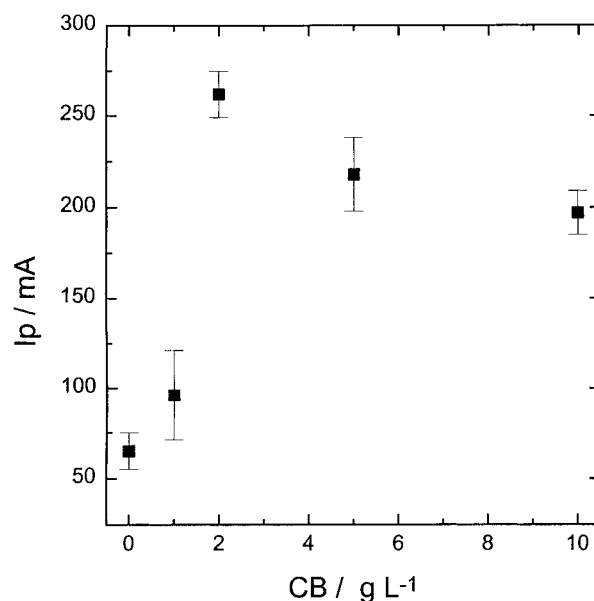


Fig. 2. Effect of carbon black content in the electrolyte on the anodic peak current for the Pani-CB composite grown up to 100 cycles in 1.0 M HCl. Data measured in $0.5 \text{ M H}_2\text{SO}_4$.

which provides additional electrodic surface for the polymer to grow on. The analysis of the micrographs in Figure 4 gives support to this consideration. The area effect does not appear at the early stages of growth because polymerization of aniline takes place on bare platinum, that is, at the Pt/electrolyte interface. Then, the initial effect of SDS is probably to partially block

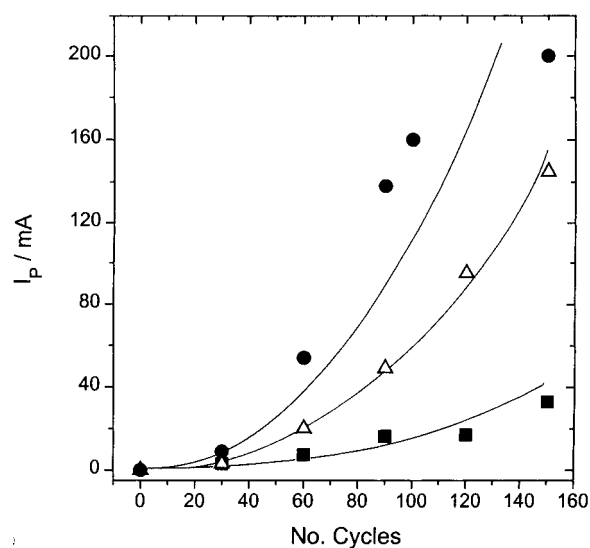


Fig. 3. Anodic peak current against number of cycles for Pani films grown with no additives (lower curve) and with additives as indicated. Synthesis electrolyte: 1.0 M HCl, 0.1 M aniline hydrochloride. Key: (■) Pani, (△) Pani + SDS and (●) Pani + SDS + CB.

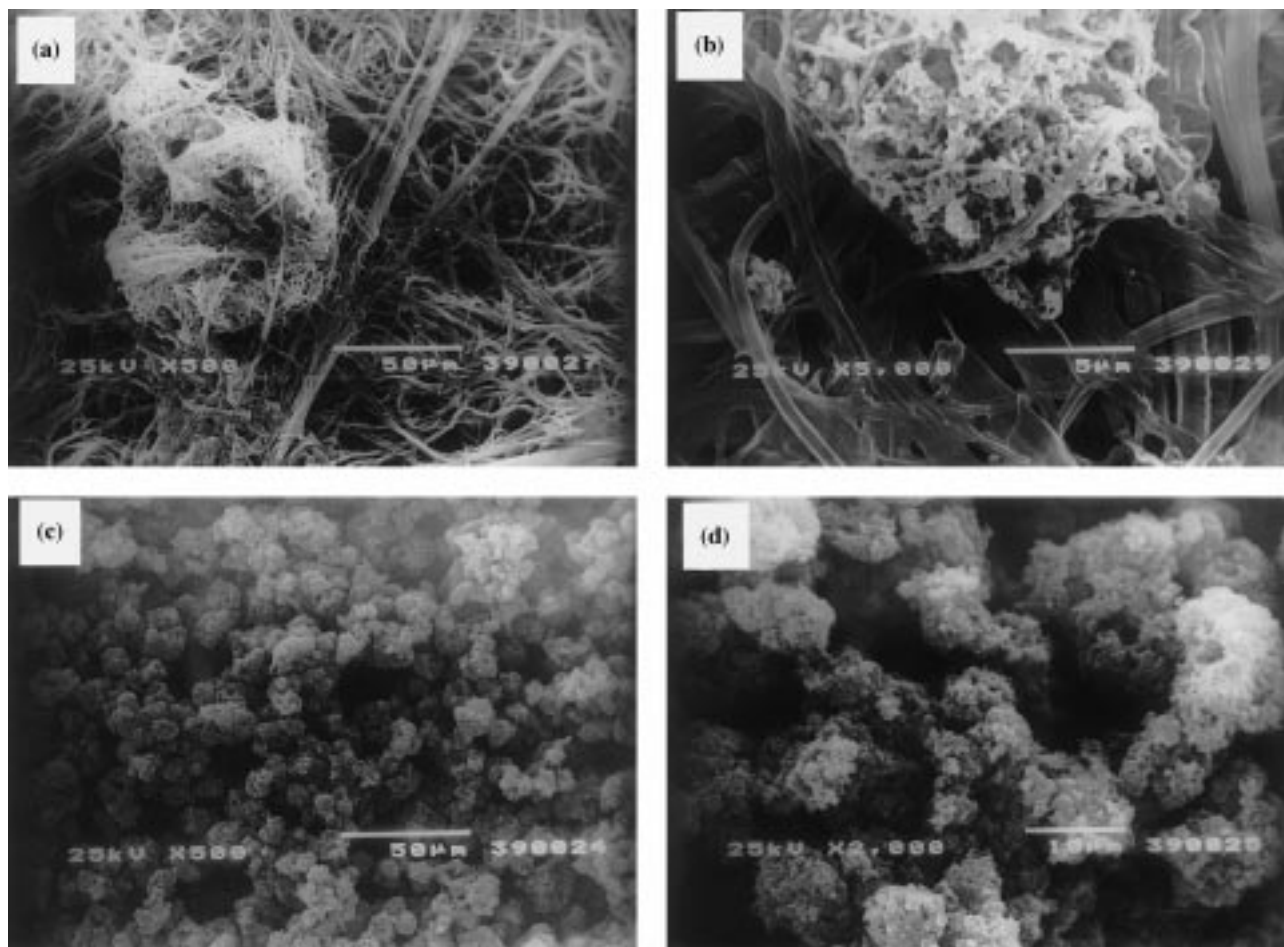


Fig. 4. SEM micrographs of Pani films with SDS (a) and (b), and Pani composite with both SDS and CB (c) and (d).

the platinum surface. At more advanced stages of polymerization, the film grows at the Pani/electrolyte interface. In this case, the carbon particles provide extra sites for polymer growth and this effect becomes more important as the process is continued. However, the presence of CB alone was not sufficient to produce this effect. On the other hand, the middle curve in Figure 3 shows that SDS in the electrolyte produces an increase in the polymerization rate. SDS is also reported to improve the stability and electroactivity of polypyrrol films [16]. Related to this, Kuramoto et al. proposed that the incorporation of the polyvinyl sulphonate additive into polyaniline is irreversible [21] and the same effect was observed in the electropolymerization of bithiophene in aqueous solutions containing sodium dodecyl sulphate [22]. The morphology reported for both polymers presented globular structures, where the anion was thought to stabilize the growing structure. The same effect is presently observed for the Pani-CB composites.

Differences in the polymer morphology were found for films prepared with and without carbon black, as shown in Figure 4. The morphology of the film obtained in solutions containing aniline and SDS, without carbon black, is defined by strip-like structures (Figure 4(a) and (b)). In contrast, in the presence of carbon black, a porous globular structure is observed for the same magnifications in Figure 4(c) and (d). No carbon particles can be distinguished in the film as they are probably embedded in the polymer matrix. It is interesting to note that the presence of carbon particles has such a profound effect on the morphology of the film, since the morphology of Pani films obtained by similar electrochemical procedures is known to be strongly determined by the nature of the electrolyte or by the potential limits used during the synthesis. These parameters usually affect the nucleation and growth mechanism for the polymer formation and consequently, its morphology. On this turn, the additive SDS itself changed the fibrillar aspect usually reported for Pani prepared in HCl for a

peculiar strip-like aspect, indicating its influence on the initial steps of kinetics process as analysed above for Figure 3.

3.2. Capacity results

Figure 5 shows the shapes of complex-plane plots obtained from EIS data, for Pani-CB films measured in H_2SO_4 . At more negative potentials ($E = -0.1$ V), where polyaniline is in the reduced state, the impedance

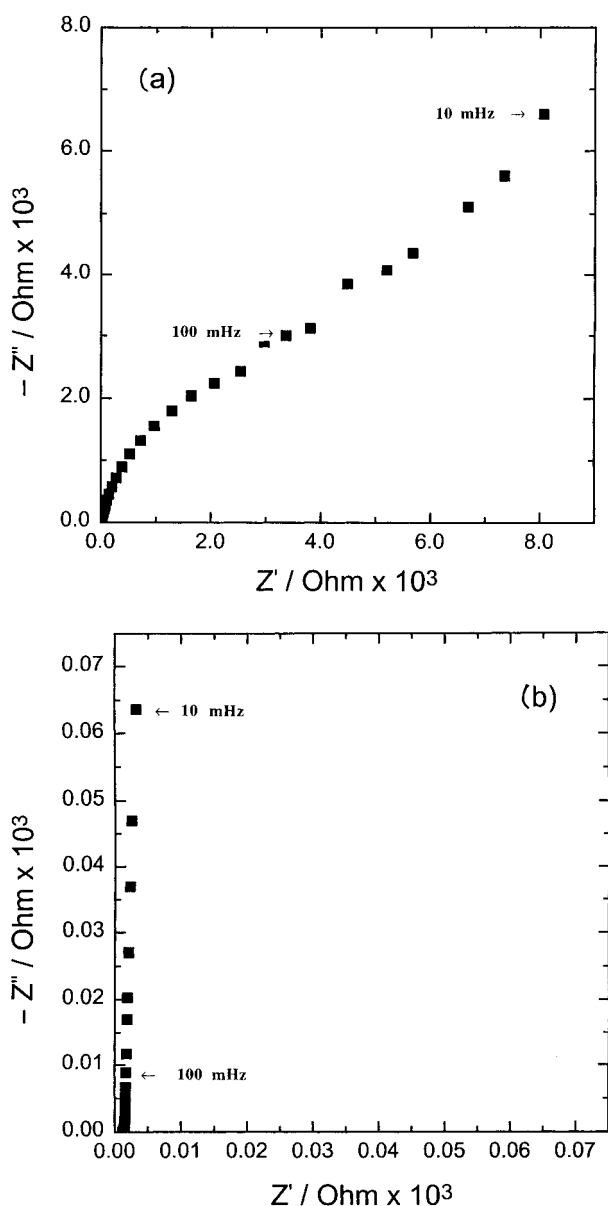


Fig. 5. Impedance spectra of a Pani-CB composite (synthesized with 1 g L^{-1} CB in the electrolyte), measured in $0.5 \text{ M H}_2\text{SO}_4$ at -0.1 V, reduced state (a) and 0.3 V, oxidized state (b).

spectrum of the composite resembles that one obtained for Pani alone in H_2SO_4 solutions [18], even though differences can be seen in the low-frequency region. The semicircle feature appearing in Figure 5(a) has been usually interpreted as an $R_s(R_p C_p)$ equivalent circuit [18], where R_s is the series ohmic resistance of the system (film plus electrolyte), R_p is the parallel charge transfer resistance and C_p is the double-layer capacitance. As the potential is made more positive, the semicircle becomes smaller and the polymer film tends to behave like a capacitor in series with R_s (Figure 5(b)). As these results are essentially in agreement with those observed for a pure Pani film, the presence of carbon particles do not seem to modify the intrinsic electronic properties of Pani in the composite.

Nevertheless, as can be seen in Figure 6, the capacity values obtained for the conducting composite in the capacitive region of the spectra, using the same method as reported before [18], are of about 250 mF for the more positive potentials (or 125 mF cm^{-2} considering the Pt substrate area), much larger than those corresponding to the pure Pani film formed during the same number of potentiodynamic cycles. This increase in capacity can be assigned to a larger film/electrolyte interface for the highly porous composite and to additional contributions of the carbon particles. However, rigorous comparisons cannot be made if film thicknesses and real areas are not precisely known. Additional information can be taken from the micrograph in Figure 7, which gives an idea of the composite

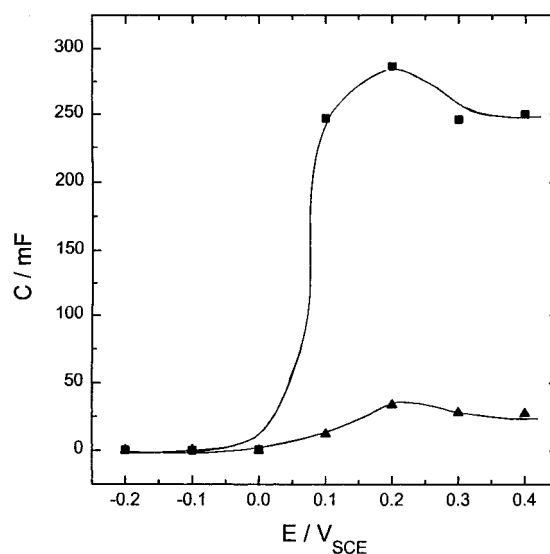


Fig. 6. The capacitance as a function of the applied potential for a Pani-CB film synthesized with 1 g L^{-1} CB in the electrolyte and for a Pani film without the additives. Key: (■) Pani CB and (▲) Pani.

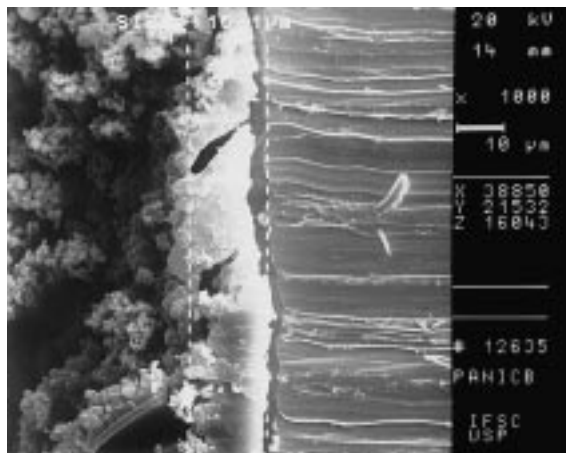


Fig. 7. Cross section micrograph of the Pt/Pani-CB interface.

thickness: for one film grown up to 100 potentiodynamic cycles, it is approximately $15\text{ }\mu\text{m}$. In spite of the film rough surface, this result allowed the determination of the ratio anodic charge/film thickness, which is about $10\text{ mC cm}^{-2}\text{ }\mu\text{m}^{-1}$, or the ratio capacity/thickness of $8\text{ mF cm}^{-2}\text{ }\mu\text{m}^{-1}$ for this series of Pani-CB composite with SDS. Compared to films of polypyrrol-SDS [23], whose capacity values are of about $0.6\text{ mF cm}^{-2}\text{ }\mu\text{m}^{-1}$, our results indicate that the Pani-CB composite has promising charge storage properties.

4. Conclusions

In this paper we demonstrate a new method of preparing composites of Pani and carbon black. Carbon black and SDS in the forming electrolyte have a pronounced effect on the kinetics of polymerization. It is possible to obtain rather porous films in much shorter time than that employed to obtain films of Pani without any additive or carbon black. The presence of carbon black particles embedded in the polymer film does not seem to modify the intrinsic electronic properties of the composite, though the substantial increase in the composite film capacity is probably due to its higher surface area.

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References

1. A.G. Mac Diarmid, J.C. Chiang, M. Halpun, W.S. Huang, S.L. Mu, N.L.D. Somarisi, W. Wu and S.I. Yaniger, *Mol. Cryst. Liq. Cryst.* **121** (1985) 173.
2. A.G. Mac Diarmid, J.C. Chiang, A.F. Ritcher and A. Epstein, *Synth. Met.* **18** (1987) 285.
3. H. Naarman, *Adv. Mater.* **2** (1990) 345.
4. M. Kaneko and H. Nakamura, *J. Chem. Soc. Chem. Commun.* (1985) 346.
5. E.W. Paul, A.J. Ricco and M.S. Wrighton, *J. Phys. Chem.* **89** (1985) 1441.
6. S.A. Chen and Y. Fang, *Synth. Met.* **60** (1993) 215.
7. A. Kitani, J. Yano and K. Sasaki, *J. Electroanal. Chem.* **209** (1986) 227.
8. B.J. Jelle and G. Hagen, *J. Electrochem. Soc.* **140** (1993) 3560.
9. M. Shaolin and K. Jinoing, *Electrochim. Acta* **40** (1995) 241.
10. P. Ocong, J.M. Leger, C. Lamy and E. Geniès, *J. Appl. Electrochem.* **19** (1996) 462.
11. V.E. Kazarinov, U.V.N. Andreev, M.A. Spitsy and A. Mayorov, *Electrochim. Acta* **35** (1990) 1495.
12. H. Tsutsumi, S. Fukuzawa, M. Ishikawa, M. Moriua and Y. Matsuda, *J. Electrochem. Soc.* **142** (1995) L168.
13. a) D.V. Jovic, T. Trisovic, D.M. Jovic and M. Vojnovic, *J. Electroanal. Chem.* **408** (1996) 149. b) A. Bhattacharya, K.M. Ganguly, A. De and S. Sarker, *Mat. Res. Bull.* **31** (1996) 527.
14. a) W. Wampler, C. Wey and K. Rajeshwar, *Materials* **7** (1995) 585. b) W. Wampler, K. Rajeshwar, R.G. Petle, R.C. Hyer and S.C. Sharma, *J. Mater. Res.* **10** (1995) 1811.
15. R.O. Loutty, *Carbon* **24** (1986) 127.
16. J.M. Pernaut, R.C.D. Peres, V.F. Juliano and M.A. De Paoli, *J. Electroanal. Chem.* **274** (1989) 225.
17. J.H. Zagal, R.R. Del Rio, B.A. Retamal and S.R. Biaggio, *J. Appl. Electrochem.* **26** (1996) 95.
18. S.R. Biaggio, C.L.F. Oliveira, M.J. Aguirre and J.H. Zagal, *J. Appl. Electrochem.* **24** (1994) 1059.
19. K. Kuramoto and E.M. Geniès, *Synth. Met.* **68** (1995) 191.
20. N. Kuramoto and A. Tomiya, *Polymer* **38** (1997) 3055.
21. N. Kuramoto, J. Mc Michelson, D.J. Mc Eloy and M. Cratzel, *J. Chem. Soc. Chem. Commun.* (1990) 1478.
22. E.A. Bazzouai, S. Aeiya, P.C. Lacaze, *Synth. Met.* **83** (1996) 159.
23. S. Panero, P. Prosperi and B. Scrosati, *Electrochim. Acta* **37** (1992) 419.